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Bonding Properties in HNO_3.HOCl.$(H_2O)_n$ clusters

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Introduction

Nitric acid and hypochlorous acid are species of atmospheric relevance [1,2]: $ClONO_2(g)+H_2O(s) \rightarrow HOCl(g)+HNO_3(s)$

Also, HOCl and HCl are strongly coupled in the atmospheric chemistry: $Cl_2(g) + H_2O(l) \leftrightarrow HOCl(l) + HCl$

Molecular clusters containing water and these acidic species are a subject of interest, especially in what concerns their bonding characteristics and spectroscopic properties.

We have studied these clusters under several theoretical facets, which include energetics, proton transfer, atomic charges and IR spectra.

Computational Details

Structure refinements and energy calculations have been carried out using Gaussian 03, with MP2/aug-cc-pVDZ methodology. This is sufficient to study bonding properties in hydrogen bond systems. In addition we have carried out single point energy calculations at MP2/aug-cc-pVTZ level on the MP2/aug-cc-pVDZ optimized geometries. Minor changes in the relative energies with respect to the double zeta results are found for just a few clusters. Atomic charges have been calculated using three different methods, referred to as Mulliken, NBO (Natural Bond Orbital) and Bader. This has allowed us to compare the corresponding results. Topologic parameters and Bader charges have been estimated using the AIMALL-AIM model, while for the NBO analyses we have used the corresponding module implemented in Gaussian 03.

Chemical intuition has been the key to design the initial cluster structures for each possible species. It is very difficult to ascertain that no other true minima exist for these systems, but if there are any, they may conceivably correspond to clusters not too different from those presented here in terms of the properties analyzed in this work. In any case, we assume that we deal with a large enough set of clusters to grant a good variety of systems and bonds.

The proton transfer parameter ρ_{PT} gives a straightforward indication of the degree of ionization of the aggregates, with negative or positive values for molecular or ionic (i.e. with fully ionized nitric acid) clusters, respectively. The definition for HNO_3 is:

$$\rho_{PT}(HNO_3) = (r_{OH} - r^{\circ}_{OH}) - (r_{H\cdots O} - r^{\circ}_{H\cdots O})$$

where r_{OH} and $r_{H\cdots O}$ indicate the interatomic distances between the shared H atom and the appropriate O atoms of the donor (HNO_3) and acceptor (H_2O or HOCl) species, that is to say, O_2NO-*H* (donor), and *H*…OH_2, *H*…*O*HCl, or, in one case *H*…*Cl*OH (acceptors) respectively. ρ_{PT} would be > 0 for an ion pair, < 0 for molecular (nonionic) complexes, and for proton sharing between both participating molecules. A similar equation applies for HOCl.

Main Results

Stable structures are found with a minimum in their potential energy surface for aggregates with three and four H_2O molecules. They are represented if Figure 1. In the most stable configurations the H atom of HNO_3 is partly donated to the O atom of HOCl (see for example, NOC3W-1 or NOC4W-1).

Our results on ρ_{PT}, electron density at the bond critical point ρ_{BCP}, atomic charges and spectroscopic properties reveal direct relationships among several of these properties. The relationship between ρ_{PT} and ρ_{BCP} is highlighted in Figure 2.

Fairly large fluctuations are calculated for the Mulliken charges, especially for molecular clusters, whereas fluctuations in the NBO or Bader charges are much more limited (see Figure 3). It is known that Mulliken charges are very dependent on the method or basis sets. Mulliken charges are more than 0.2 units smaller than the other two models for ionic clusters.

The predicted spectra present large variations in wavenumber and intensity of the main bands that depend on the bonding types, especially on which species is the acceptor of the HNO_3 proton (see Figure 4).

Finally, the HOCl clusters considered here were compared with similar aggregates containing HCl studied in a previous work [3]. We have found that the weaker acid HOCl favors a higher degree of proton sharing in HNO_3.

Summary and Conclusions

- Most clusters with the same number of water molecules are calculated within a small energy range, ~2 kcal/mol.
- In some clusters with four water molecules real proton transfer is found so that the nitric acid adopts an ionic configuration.
- For the molecular clusters studied here, ρ_{PT} values of HNO_3 range between -0.35 and -0.88 Å, with ρ_{PT} values get closer to zero (i.e. NOC3W-2, NOC4W-9) when HNO_3 donates its proton to water. Positive values between 0.30 and 0.55 are estimated for the ionic clusters.
- Calculated values for ρ_{BCP} are typical of H-bonds.
- Atomic charges do not show any correlation with the type of accepting atom of the H bond.
- The predicted spectra of these clusters display quite different characteristics which could be used to identify specific aggregates among complex spectra. For instance, clusters where HOCl is the acceptor present spectra with two strong bands in the 2500-3000 cm^{-1} region.
- The O-H vibrational mode of HNO_3 is always red-shifted with respect to the free molecule, and the shifts are larger when the acceptor is H_2O.
- A comparison of $HNO_3 \cdot HOCl \cdot (H_2O)_n$ and $HNO_3 \cdot HCl \cdot (H_2O)_n$ clusters with a similar structure shows that they follow in general the same trend in terms of ρ_{PT} and ρ_{BCP} values.

HNO_3.HOCl.$(H_2O)_4$ clusters

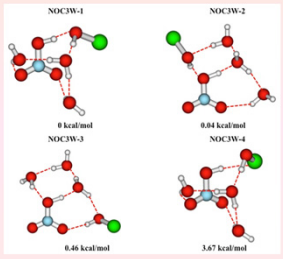
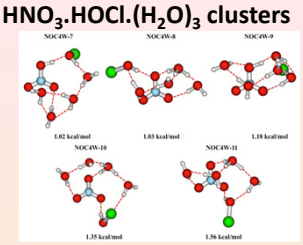


Figure 1. Clusters and relative energies

HNO_3.HOCl.$(H_2O)_3$ clusters



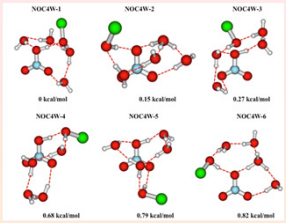


Figure 2. Proton transfer vs electron density at critical point

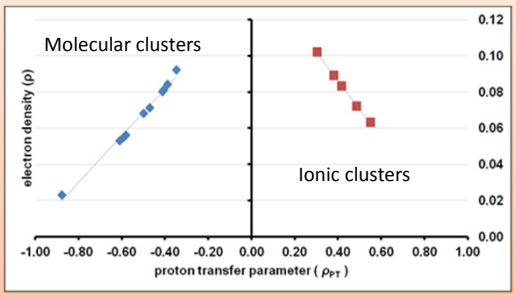


Figure 3. Comparison of atom charges models

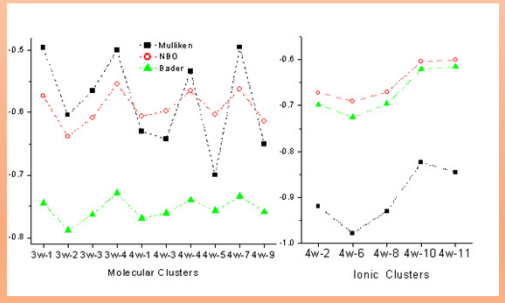
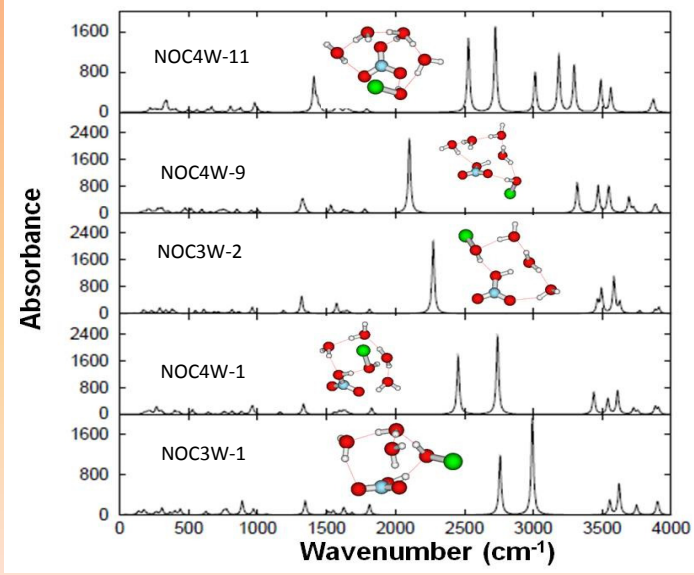


Figure 4. Prediction of IR spectra



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